(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: 0 309 286 A2

(12) EUROPEAN PATENT APPLICATION

(21) Application number: 88308889.0

(22) Date of filing: 23.09.88

(51) Int. Cl.⁴: H 01 B 1/00
C 09 D 5/24, C 09 D 3/72,
C 08 J 7/04

(30) Priority: 25.09.87 JP 241653/87

(43) Date of publication of application:
29.03.89 Bulletin 89/13

(84) Designated Contracting States:
AT BE CH DE ES FR GB GR IT LI LU NL SE

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(54) Conductive agent for electrostatic coating of plastics and electrostatically coated plastic moldings.

(57) A composition and method for effective electrostatic coating on a plastic article uses an electrically conductive agent comprising a polyurethane and an electrically conductive filler such as inorganic fine powder and organic substances.

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Description

CONDUCTIVE AGENT FOR ELECTROSTATIC COATING OF PLASTICS AND ELECTROSTATICALLY COATED PLASTIC MOLDINGS

The present invention relates to a conductive agent usable as a primer in the electrostatic coating of highly crystalline plastics having a poor polarity. In particular, the present invention relates to a conductive agent which surely increases the electrostatic coating efficiency, which exhibits a high wetting power against the plastics to be coated and which does not inhibit the adhesion of the electrostatic coating film, as well as plastic moldings electrostatically coated by using this conductive agent.

[Prior Art]

As is well known, the electrostatic coating method comprises applying a high-voltage DC between an object and a spray-coating apparatus to form a line of electrostatic force between them and adhering a charged paint in the form of a spray to the surface of the object along the line of electrostatic force. The paint consumption loss is far lower (about 1/2-fold) than that of an ordinary spray-coating method. Another advantage of this method is that a coating film can be formed uniformly all over the object including shadows. The electrostatic coating method is, therefore, widely employed. When the electrostatic coating method is employed for coating a non-conductive substance such as a non-conductive plastic, a conductive agent is applied as a primer to the object in order to make it conductive. Namely, the conductive agent is applied to the surface of the non-conductive object to form a conductive film and then this film is charged to conduct the electrostatic coating.

The conductive agents usable for the above-described purpose include, for example, various amphoteric, conductive organic substances such as quaternary ammonium salts, as well as cationic, anionic and nonionic conductive organic substances. They are suitably diluted with a suitable solvent and the solution is applied to the surface of the object to form an extremely thin primer layer prior to the electrostatic coating. However, known conductive agents are prepared mainly for the purpose of increasing the electrostatic efficiency but the effects thereof on the adhesion of the electrostatic coating film to the object have scarcely been studied yet. In the course of the investigations of methods of electrostatically coating highly crystalline plastics having a very low polarity and only a poor adhesion (hereinafter referred to as the difficulty coatable plastics in some cases) such as polyacetal and polyester resins, the inventors encountered the following problems. Although it is indispensable to form previously a conductive film as the primer layer also when the difficulty coatable plastics are electrostatically coated, the conventional conductive agents have a quite poor adhesion to such plastics. Even when the affinity of an electrostatic paint for the plastic is improved by suitably adjusting the materials for the paint, a film having a conductive layer is easily peeled off from the plastic. Thus, no satisfactory adhesion could be obtained heretofore.

The inventors have made investigations for the purpose of solving the above-described problems. An object of the present invention is to develop a conductive agent capable of effectively exhibiting its essential functions, having an excellent property of wetting the difficulty coatable plastics and also capable of forming a primer layer which firmly adheres an electrostatic coating film to the surface of an object. Another object of the present invention is to provide electrostatically coated moldings in which the electrostatic coating layer is firmly adhered by using such a conductive agent.

(Summary of the Invention)

The present invention provides a conductive agent for electrostatic coating which comprises as the main constituents:

(A) a polyurethane resin and

(B) a conductive inorganic fine powder and/or a conductive organic substance, and electrostatically coated plastic moldings prepared by the electrostatic coating by using this conductive agent.

The invention provides an electrically conductive composition to use for the electrostatic coating on a plastic article, which comprises (A) a polyurethane resin and (B) an electrically conductive inorganic fine powder and/or an electrically conductive organic substance.

It is preferable that the component (B) is contained in the composition in so effective an amount that the surface resistance may be not larger than 10^{13} ohms.cm.

The invention provides a method for electrostatically coating a plastic article which comprises first coating the article with the composition as defined above and then effecting the electrostatic coating thereon. It adds a plastic article obtained by the method as defined above.

The minimum requirement for the properties of the conductive agent for electrostatic coating are as follows:

(1) it is capable of forming a highly conductive film so as to increase the electrostatic adhesion efficiency in the electrostatic coating step,

(2) the wettability therewith of an object is good and a prime layer formed from the conductive agent has an excellent adhesion to both of the object and electrostatic coating film, and no film is peeled off, and

(3) the conductive agent neither modifies nor deteriorates the object or components of the film formed by the electrostatic coating method. Due consideration has been given to the requirements (1) and (3) and they have been satisfied considerably in the prior art. However, no detailed investigations were made on the requirement

(2), since most of the objects were polar substances and their adhesion to the conductive agent was substantially not at stake. After investigations of methods of electrostatic coating of the above-described difficulty coatable plastics such as polyacetal resin, polyethylene terephthalate, polybutylene terephthalate and aromatic polyesters, the inventors have found that the above-described property (2) required of the conductive agent usable as the primer is quite important and that when this property is unsatisfactory, a layer formed by electrostatic coating is easily peeled off to make a coated article valueless. After intensive investigations made for the purposes of elucidating the mechanism of the reduction in the adhesion and developing a process for overcoming the defects, the inventors have found that:
(1) the adhesion is reduced because a conductive organic substance which is a main component of the conductive agent has a surface-activating effect and, therefore, when this substance is present on the surface of an object, the adhesion is seriously inhibited,
(2) when a suitable amount of a polyurethane resin is incorporated in the conductive agent comprising the conductive organic substance, the adhesiveness and film-forming property of the polyurethane resin per se are effectively exhibited and, in addition, the conductive organic substance is entrapped in the polyurethane resin to control the adhesion-inhibiting property due to the surface-activating effect of the organic substance in the film-forming step,
(3) the polyurethane resin is quite highly adhesive to the film formed by the electrostatic coating and, therefore, the difficulty coatable plastics are firmly adhered to the layer formed by the electrostatic coating method via the conductive coating layer containing the polyurethane resin, and
(4) materials capable of imparting a conductivity include inorganic conductive fine powders in addition to ordinarily used conductive organic substances soluble in a solvent and particularly when both of them are used together, the physical properties of the conductive coating layer are further improved and the adhesion of the electrostatic coating layer is further improved. After further investigations made on the basis of these findings, the inventors have completed the present invention.

Now, the description will be made on the components of the conductive agent of the present invention.

As described above, the polyurethane resin acts as the conductive film-forming component. This resin is adherable to both of the difficulty coatable plastics and the electrostatic coating layer. The conductive organic substance is entrapped in the polyurethane resin and, therefore, the adhesion-inhibiting property of the organic substance is controlled. When the conductive inorganic fine powder is used, the polyurethane resin acts also as a vehicle to uniformly distribute the fine powders in the coating layer. In view of all of these effects, the effective polyurethane resin has an average molecular weight of about 2,000 to 10,000, and more preferably about 4,000 to 7,000.

As a matter of course, the conductive inorganic fine powder and conductive organic substance are components used for making the primer layer conductive (surface resistance: below about $10^{13}\ \Omega\cdot$cm) in the electrostatic coating process. The conductive inorganic fine powders include, for example, conductive metal powders (including short fibers), metal-coated fillers (such as nickel-plated mica and nickel-plated glass balloons) and conductive fillers (such as conductive titanium oxide, conductive zinc white, conductive antimony trioxide and graphite). The conductive inorganic fine powder used as the conductive film constituent has preferably a very small particle size and a large specific surface area. Usually fine particles having a particle diameter of smaller than about 20 µm are used. The conductive organic substances include known ones such as solvent-soluble cationic, amphoteric, nonionic and anionic conductive organic substances. They are not particularly limited. The most common conductive organic substances are quaternary ammonium salts, alkylbetaines, alkylamines, salts of alkyl sulfates, etc.

Though the conductive inorganic fine powder and the conductive organic substance can be used solely, it is most preferred to use a combination of suitable amounts of them for the following reasons. When the conductive inorganic fine powder is used solely, it is difficult to increase the conductivity and a considerably large amount thereof is necessitated for obtaining a satisfactory conductivity. As a result, the transparency of the coating film is reduced unfavorably. On the contrary, when the conductive organic substance is used, a transparent, highly conductive coating layer is formed but the coating layer per se is weak and in case an external force is applied in a peeling direction thereto, a cohesive failure is often caused in the conductive coating layer per se. When a combination of both of them is used, the coating layer reinforcing effect of the conductive inorganic fine powder and the excellent conductivity of the conductive organic substance are effectively exhibited. By these effects coupled with the excellent adhesion and film-forming property of the polyurethane resin, the conductive coating layer thus obtained has quite excellent conductivity, adhesion and physical properties.

The compounding ratio of the conductive substance to the polyurethane resin is not particularly limited, since it varies depending on the kind of the conductive substance, molecular weight of the polyurethane resin and physical properties and conductivity required of the conductive coating layer. Usually, however, the amounts of them used are as follows:

(A) 90 to 50 parts by weight of the polyurethane resin and 10 to 50 parts by weight of the inorganic fine powder when this powder is used singly,

(B) 50 to 97.5 parts by weight of the polyurethane resin and 50 to 2.5 parts by weight of the conductive organic substance when this substance is used singly, and

(C) 50 to 30 parts by weight of the polyurethane resin, 10 to 50 parts by weight of the conductive inorganic fine powder and 4 to 50 parts by weight of the conductive organic substance when a

combination of the two conductive substances is used.

The conductive coating layer forming components are used in a state diluted to a concentration of usually about 60 to 95%, more usually about 70 to 90%, with a ketone solvent such as methyl ethyl ketone or an alcohol solvent such as isopropyl alcohol.

If necessary, the conductive agent of the present invention can contain, in addition to the above-described components, additives such as a lubricant dispersant, precipitation inhibitor, leveling agent and colorant.

The conductive agent of the present invention is used for making the surface of a con-conductive plastic material conductive so that the electroconductive coating thereof is made possible. A thickness of the conductive layer of as thin as about 0.1 to 1 µm will suffice. The most ordinary coating method is air spraying, though immersion coating, brush coating or roll coating can also be employed. When the layer of the conductive agent is thus formed on the plastic molding, a firm coating film can be formed thereon by an ordinary electrostatic coating method to obtain the product having quite excellent appearance and surface profile.

The conductive agent of the present invention having the above-described construction has a conductivity sufficient for the electrostatic coating and also has an excellent adhesion to the difficulty coatable plastics such as polyacetal or polyester resin. According to the present invention, problems such as the peeling of a coating film of an electrostatically coated plastic and other disadvantages caused by the peeling are solved. The advantages of the electrostatic coating can be obtained in the coating of even the plastic material which cannot be easily coated. Excellent electrodeposition products can thus be provided.

[Examples]

Conductive agents having compositions shown in Tables 1-(1) and 1-(2) were prepared. Each of them was applied to polyacetal resin plate, polyethylene terephthalate plate and polybutylene terephthalate plate by air spraying so that the film thickness after drying would be 1.0 ± 0.3 µm, 5 ± 0.5 µm, 10 ± 2 µm or 15 ± 5 µm, respectively, the thickness being varied depending on the kind thereof, and then air-dried.

The conductive layer forming components shown in Table 1 were as follows:

polyurethane resin: "Barnok 16-416" (a product of Dainippon Ink & Chemicals, Inc.),
quaternary ammonium salt: " Conagent H-10" (a product of Yutaka Shosha),
"BYK ES-80" (a product of BYK Chemie), and
"Electrostripper A" (a product of Kao Corporation),
cationic conductive organic substance: "Electrostripper QN" (Kao Corporation),
nonionic conductive organic substance: "Electrostripper EA" (Kao Corporation),
anionic conductive organic substance: "Electrostripper PC" (Kao Corporation),
Ni-plated mica: "EC-325" (Kuraray Co., Ltd.),
conductive antimony trioxide: "W-10" (Mitsubishi Metal Corporation),
conductive titanium dioxide: "500-W" (Ishihara Sangyo Kaisha Ltd.),
conductive zine white: "23-K" (Hakusui Kagaku Co.), and
graphite: POG-10 (Sumitomo Chemical Co., Ltd.)

Table 1-(1)

(unit: wt. %)

Experiment No.	1	2	3	4	5	6	7	8	9	10
Polyurethane resin	6.5	6.3	6.2	9.0	6.5	6.5	6.3	6.2	9.0	6.5
Conductive inorganic fine powder										
Ni-plated mica	6.5	6.3	6.2	2.0	6.5	-	-	-	-	-
conductive antimony trioxide	-	-	-	-	-	6.5	6.3	6.2	2.0	6.5
conductive titanium dioxide	-	-	-	-	-	-	-	-	-	-
conductive zinc white	-	-	-	-	-	-	-	-	-	-
Conductive organic substance										
amphoteric conductive agent	1.0	4.1	5.3	9.0	6.5	1.0	4.1	5.3	9.0	6.5
nonionic conductive agent	-	-	-	-	-	-	-	-	-	-
cationic conductive agent	-	-	-	-	-	-	-	-	-	-
anionic conductive agent	-	-	-	-	-	-	-	-	-	-
Solvent (total)	(86.0)	(84.9)	(82.3)	(80.0)	(80.5)	(86.0)	(84.9)	(82.3)	(80.0)	(80.5)
acetone	43.0	42.5	41.1	40.0	40.3	40.3	42.5	41.1	40.0	40.3
MEK	21.5	21.2	20.6	20.0	20.1	20.1	21.2	20.6	20.0	20.1
IPA	21.5	21.2	20.6	20.0	20.1	20.1	21.2	20.6	20.0	20.1
Total	100	100	100	100	100	100	100	100	100	100

Table 1-(2)

(unit: wt. %)

Experiment No.	11	12	13	14	15	16	17	18	19	20	21	22
Polyurethane resin	11.7	5.0	5.5	5.5	11.7	5.0	11.7	5.0	18.0	10.0	18.0	10.0
Conductive inorganic fine powder												
Ni-plated mica	-	-	-	-	-	-	-	-	-	-	-	-
conductive antimony trioxide	-	-	-	-	-	-	-	-	-	-	-	-
conductive titanium dioxide	-	-	-	-	-	-	-	-	2.0	10.0	-	-
conductive zinc white	-	-	-	-	-	-	-	-	-	-	2.0	10.0
Conductive organic substance												
amphoteric conductive agent	0.3	5.0	2.8	3.6	-	-	-	-	-	-	-	-
nonionic conductive agent	-	-	-	-	0.3	5.0	-	-	-	-	-	-
cationic conductive agent	-	-	-	-	-	-	0.3	5.0				
anionic conductive agent												
Solvent (total)	(88.0)	(90.0)	(91.7)	(90.9)	(88.0)	(90.0)	(88.0)	(90.0)	(80.0)	(80.0)	(80.0)	(80.0)
acetone	44.0	45.0	45.9	45.5	44.0	45.0	44.0	45.0	40.0	40.0	40.0	40.0
MEK	22.0	22.5	22.9	22.7	22.0	22.5	22.0	22.5	20.0	20.0	20.0	20.0
IPA	22.0	22.5	22.9	22.7	22.0	22.5	22.0	22.5	20.0	20.0	20.0	20.0
Total	100	100	100	100	100	100	100	100	100	100	100	100

The plastic plates on which the conductive layer had been thus formed were then subjected to the electrostatic coating under conditions which will be described below. A uniform coating film could be formed by the electrostatic coating method in all cases. The adhesion of the electrostatic coating film to the plastic plate was quite excellent and no peeling was recognized at all in the cross-cut adhesion test with a tape.

On the contrary, when the polyurethane resin-free conductive agent was used, the electrostatic coating film was easily peeled off from the conductive film surface, though the electrostatic coating per se could be conducted easily.

Electrostatic coating agents:
(1) Primer: Primer DP-A (patent pending) for Duracon (trade name),
(2) Face coating: Amilac 371-531 White (Kansai Paint Co., Ltd.).

Electrostatic painting conditions:
R-E-A gun (Ransburg Gema Co., Ltd.)

Cross-cut adhesion test:
1 mm cross-hatching; peeling with a cellophane tape (100 squares of a size of 1 x 1 mm).

Claims

1. An electrically conductive composition to use for the electrostatic coating on a plastic article, which comprises (A) a polyurethane resin and (B) an electrically conductive inorganic fine powder and/or an electrically conductive organic substance.

2. A composition as claimed in claim 1, in which the component (B) is contained in so effective an amount that the surface resistance may be not larger than 10^{13} ohms.cm.

3. A composition as claimed in claim 1 or claim 2, in which the polyurethane resin (A) has an average molecular weight of 4000 to 7000.

4. A composition as claimed in any preceding claim, in which any conductive inorganic fine powder has a particle size of smaller than 20µm (micrometres).

5. A composition as claimed in any preceding claim in which the conductive inorganic fine powder and the conductive organic substance are used in combination.

6. A method for electrostatically coating a plastic article, which comprises first coating the article with the composition as defined in any preceding claim and then effecting the electrostatic coating thereon.

7. A coated plastic article obtained by the method as defined in claim 6.